

タンタル上のアルキン配位子交換反応の機構研究

岡山大学

大学院自然科学研究科

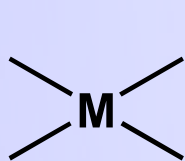
押木俊之 (おしきとしゆき)



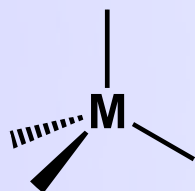
Oshiki, T.; Yamada, A.; Kawai, K.; Arimitsu, H.; Takai, K. *Organometallics* **2007**, 1, 173.

遷移金属錯体の分子構造

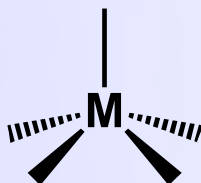
4配位錯体



平面四角形

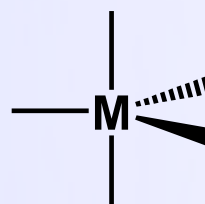


四面体形



正方錐形

5配位錯体



三方両錐形

6配位錯体

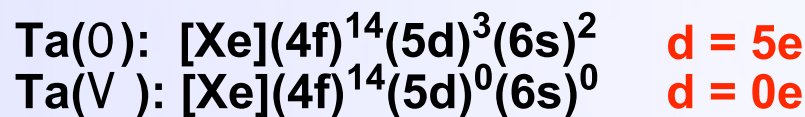
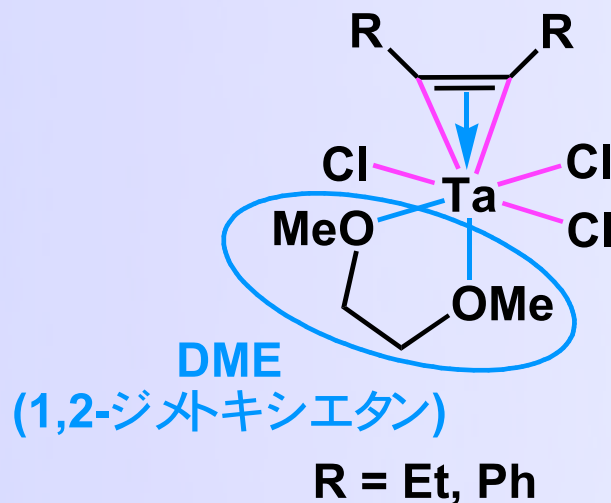


八面体形



三角柱形

タンタルーアルキン錯体

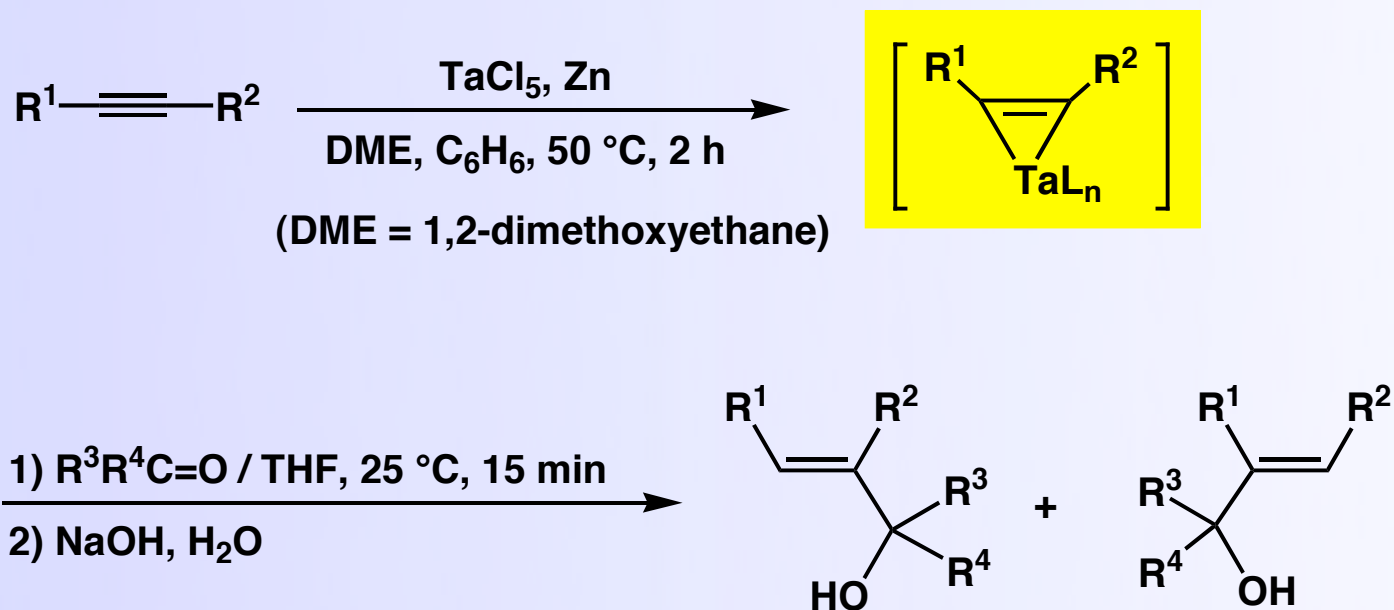


タンタルd⁰16電子錯体

d電子	0	= 0e
アルキン配位子	2e × 3	= 6e
Cl配位子	2e × 3	= 6e
DME配位子	2e × 2	= 4e

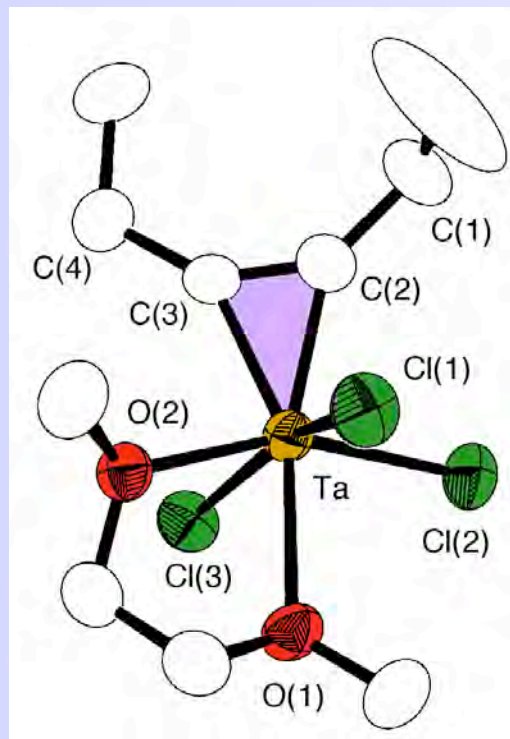
Kataoka, Y.; Miyai, J.; Oshima, K.; Takai, K.; Utimoto, K. *J. Org. Chem.* **1992**, 57, 1973.
Oshiki, T.; Tanaka, K.; Yamada, J.; Ishiyama, T.; Kataoka, Y.; Mashima, K.; Tani, K.;
Takai, K. *Organometallics* **2003**, 22, 464.

Reactions between Tantalum-Alkyne Complexes and Carbonyl Compounds



Kataoka, Y.; Miyai, J.; Oshima, K.; Takai, K.; Utimoto, K. *J. Org. Chem.* **1992**, 57, 1973.

Molecular Structure of TaCl₃(η^2 -EtC \equiv C η)(dme)

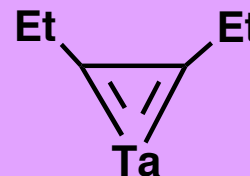
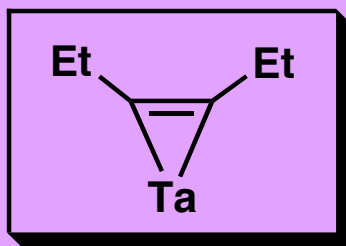
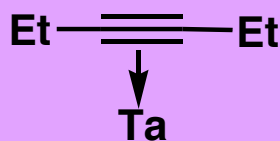


Bond Distances and Angles

Ta—O(1)	2.355(6) Å	Ta—Cl(1)	2.383(2) Å
Ta—O(2)	2.196(6)	Ta—Cl(2)	2.386(2)
Ta—C(2)	2.046(9)	Ta—Cl(3)	2.417(2)
Ta—C(3)	2.102(7)	C(2)—C(3)	1.39(1)
\angle C(1)—C(2)—C(3)	140.6(7)°		
\angle C(2)—C(3)—C(4)	142.9(9)		

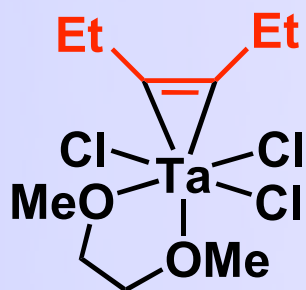
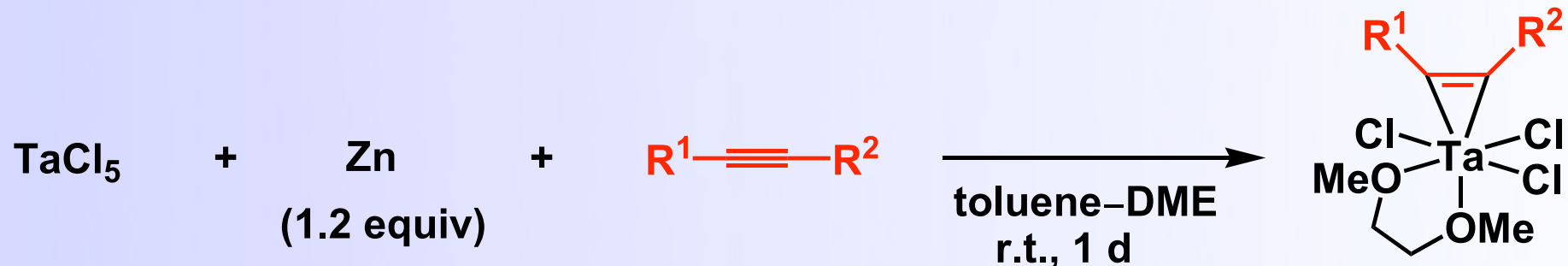
¹³C NMR (CD₂Cl₂): δ 256.0 (C(2) and C(3))

IR (nujol/CsI): 1622 (ν C(2) \equiv C(3)) cm⁻¹

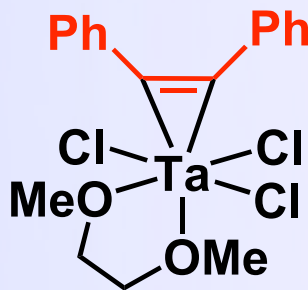


Oshiki, T.; Tanaka, K.; Yamada, J.; Ishiyama, T.; Kataoka, Y.; Mashima, K.; Tani, K. Takai, K. *Organometallics* **2003**, 22, 464

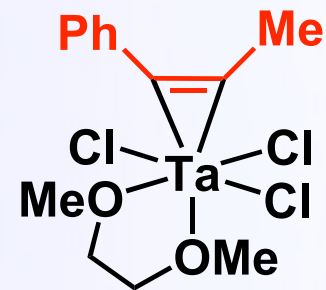
タンタル–アルキン錯体の合成法



65%

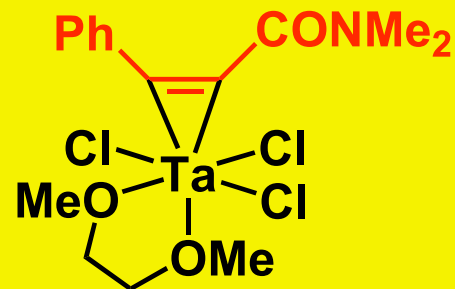
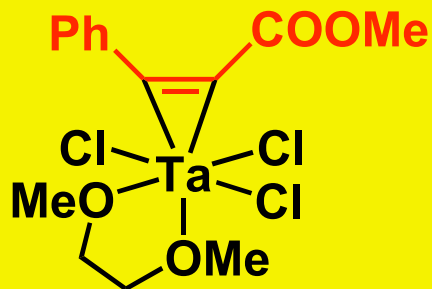


75%

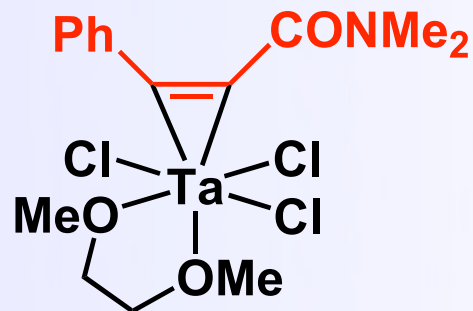
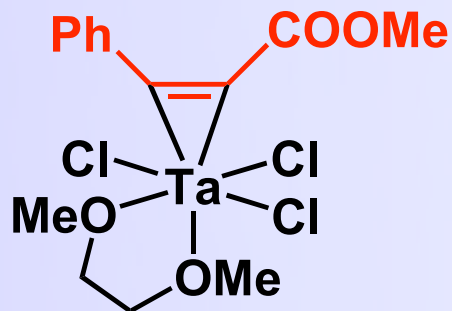


57%

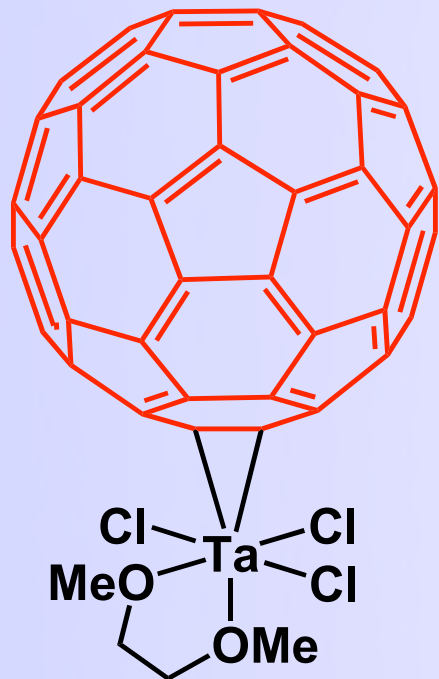
この方法では単離できない錯体



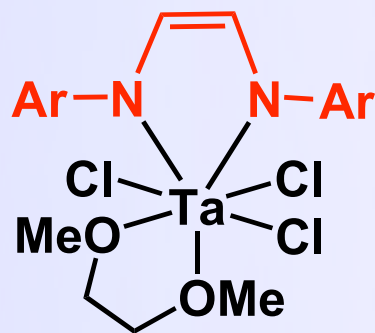
新規タンタル錯体の合成と単離への可能性



novel alkene complexes

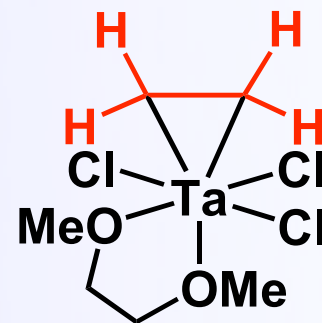


fullerene complex



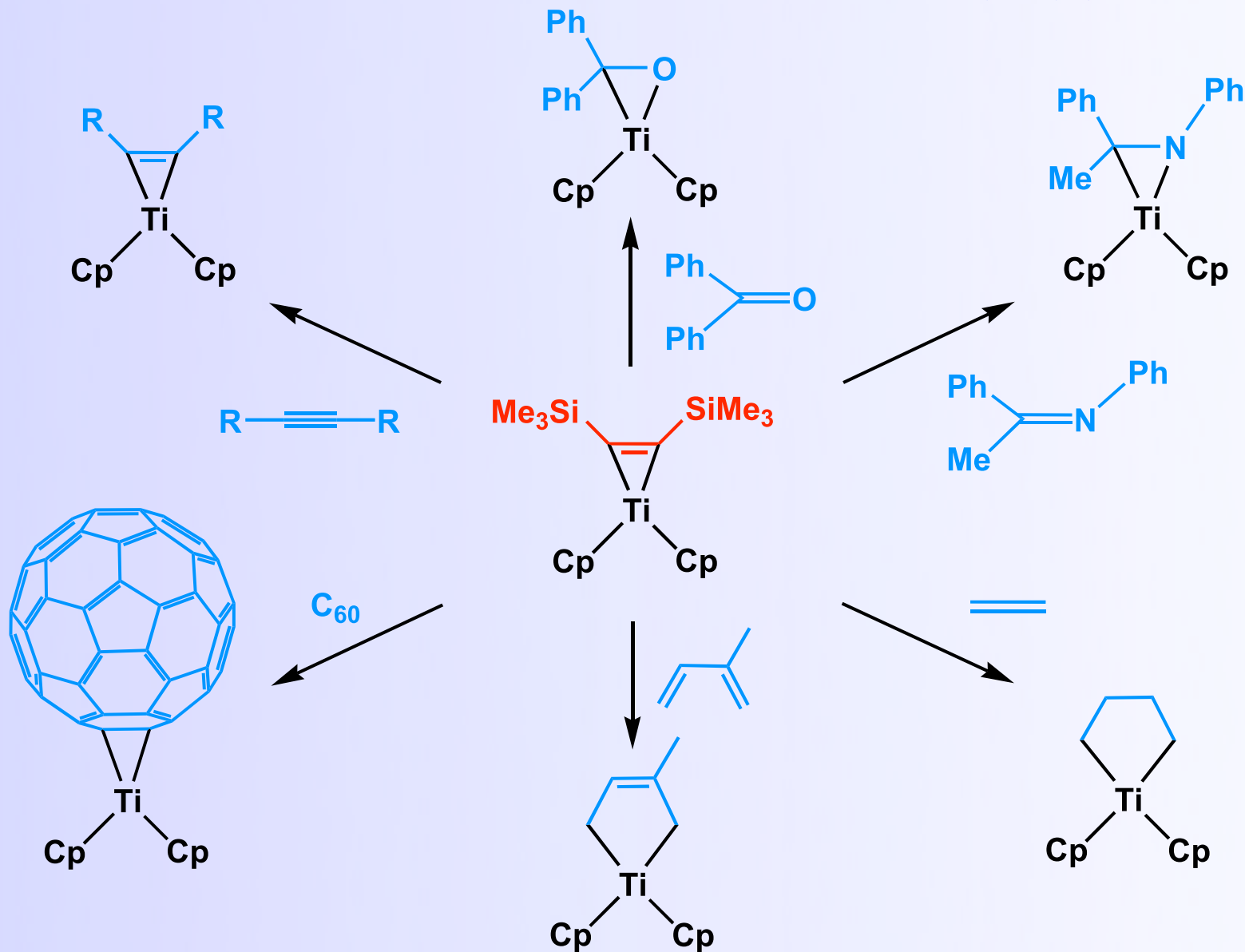
(Ar = 4-MeOC₆H₄)

diazadiene complex



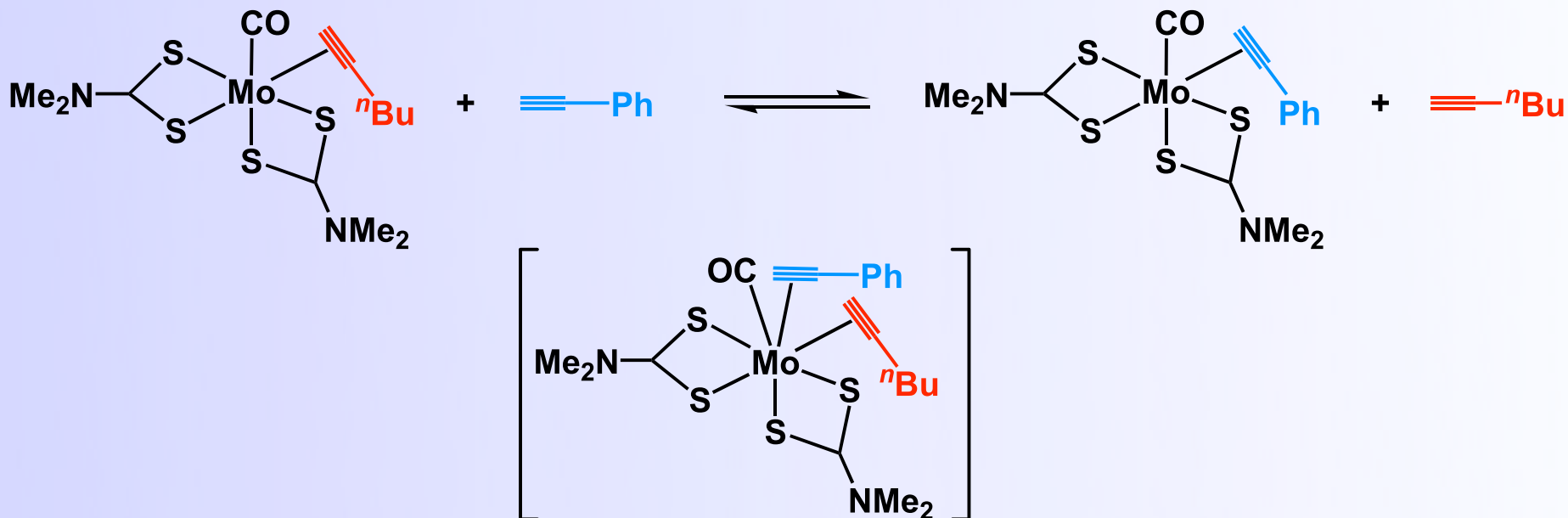
ethylene complex

チタン-シリルアルキン錯体のアルキン交換反応

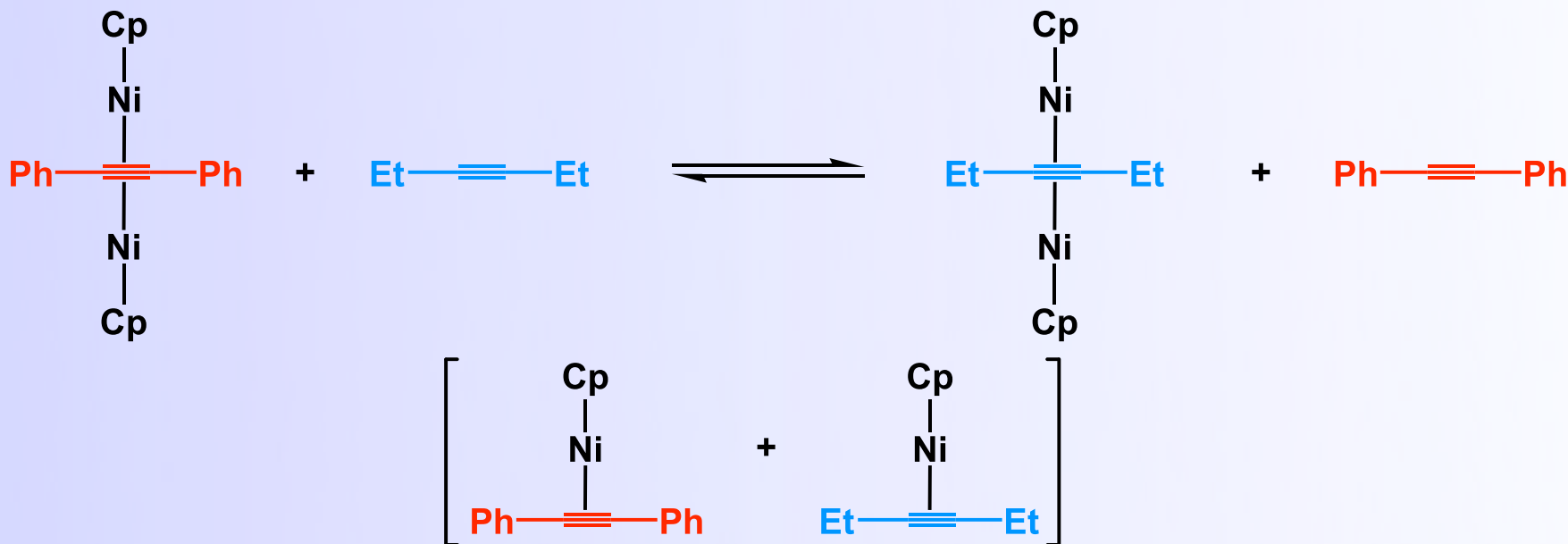


Rosenthal, U.; Burlakov, V. V.; Baumann, W. P.; Spannenberg, A. *Organometallics* **2003**, 22, 884.
 Burlakov, V. V.; Usatov, A. V.; Lyssenko, K. A.; Antipin, M. Y.; Novikov, Y. N.; Shur, V. B. *Eur. J. Inorg. Chem.* **1999**, 1855.

他の金属のアルキン交換反応

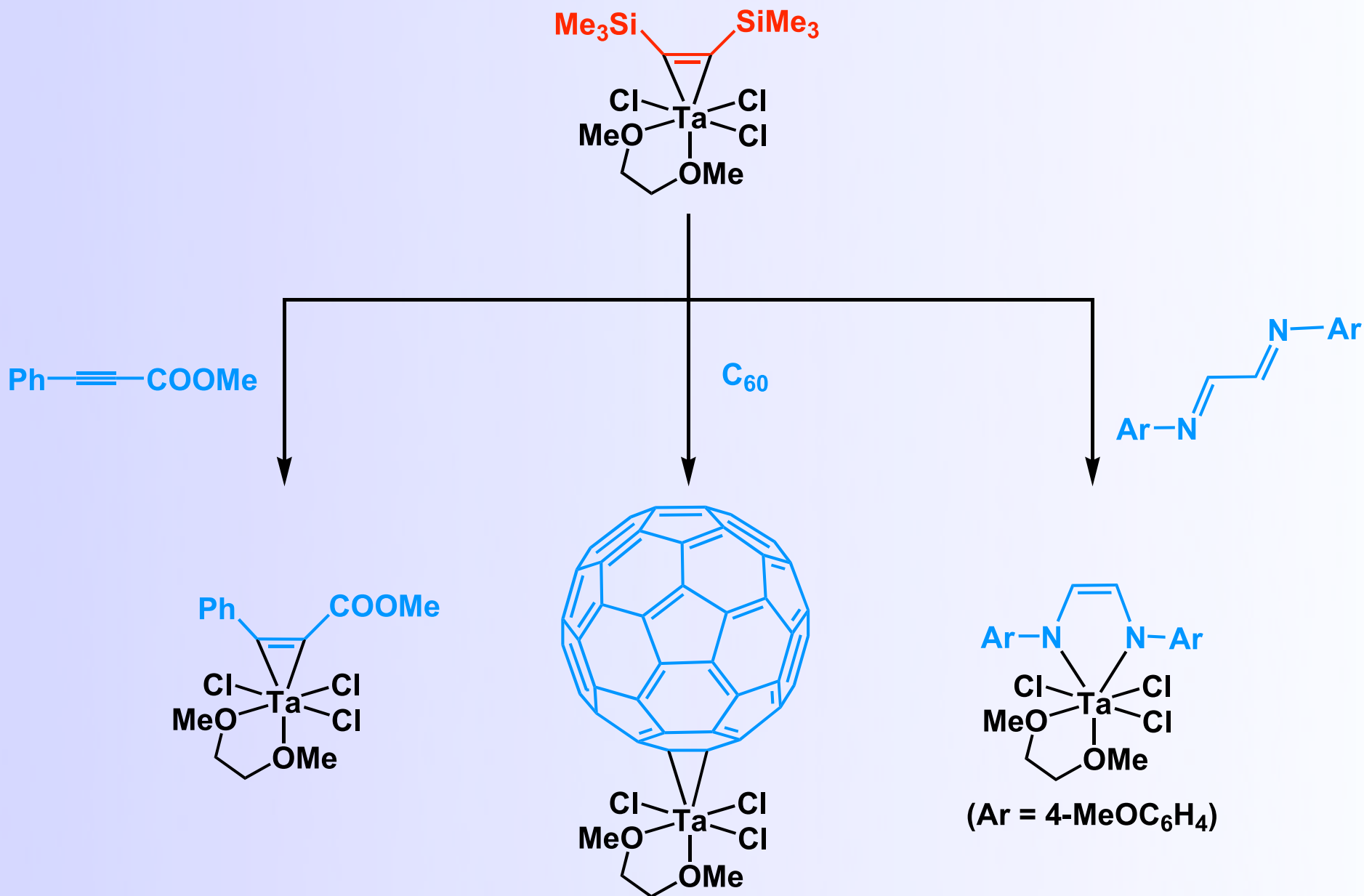


Herrick, R. S.; Leazer, D. M.; Templeton, J. L. *Organometallics* **1983**, 2, 834.



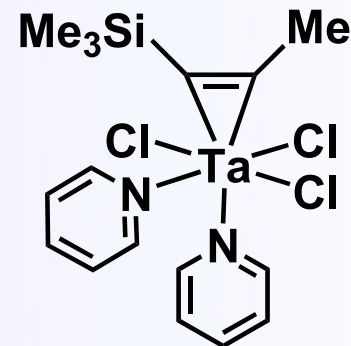
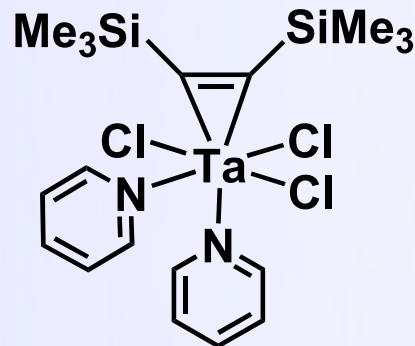
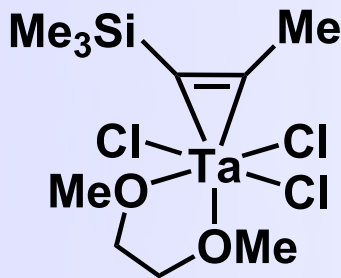
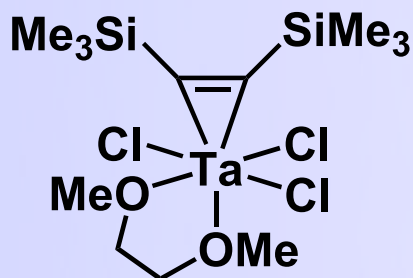
Slater, S. S.; Muetterties, E. L. *Inorg. Chem.* **1981**, 20, 1604.

新規タンタル錯体の合成計画



研究内容

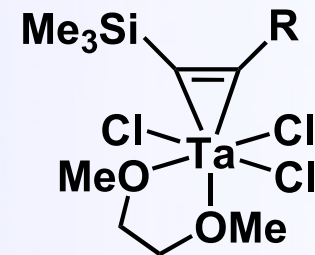
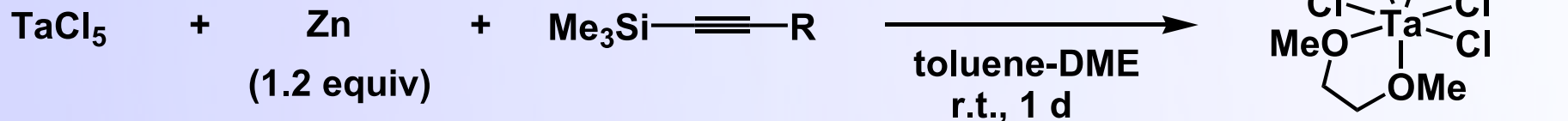
・タンタルーシリルアルキン錯体の合成とその反応性



・アルキン交換反応の速度式と活性化パラメータの算出

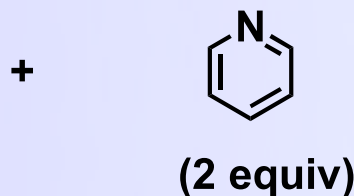
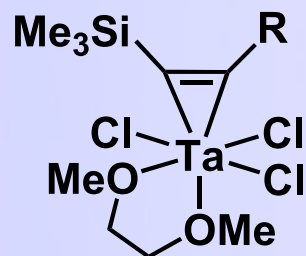
・アルキン交換反応の新規錯体合成への応用

タンタルーシリルアルキン錯体の合成

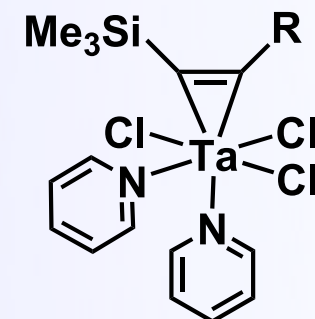


A (R = SiMe₃, 28%)

B (R = Me, 59%)

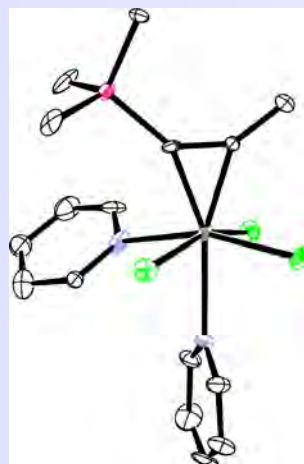
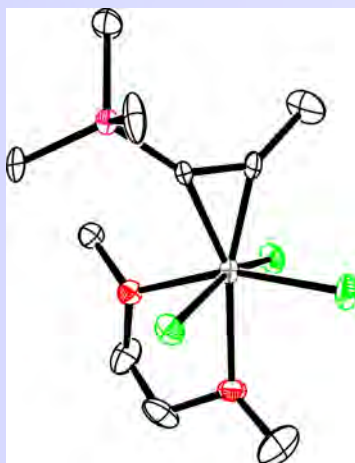


toluene
r.t., 1 d



C (R = SiMe₃, 60%)

D (R = Me, 65%)

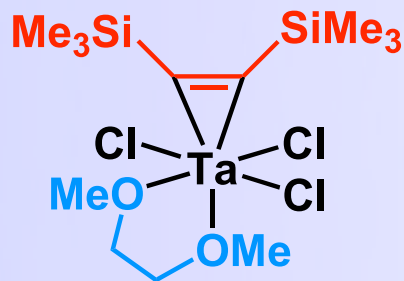
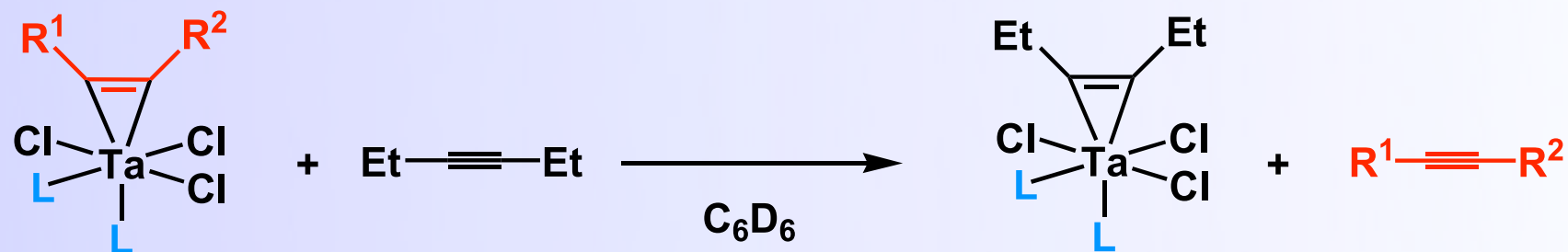


B と D の分子構造

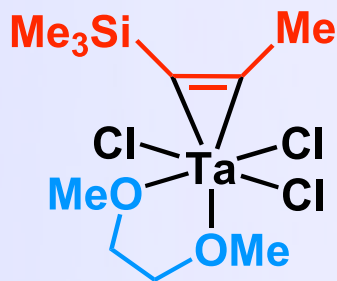
アルキン配位子のスペクトルデータ

	$^{13}\text{C}\{^1\text{H}\}$ NMR (ppm)	IR (cm ⁻¹)
<u>A</u>	265.9	1581
<u>B</u>	252.8, 262.6	1640
<u>C</u>	265.1	1606
<u>D</u>	250.6, 264.4	1644

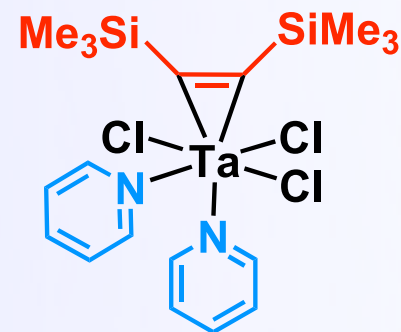
タンタルーアルキン錯体と内部アルキンの反応性



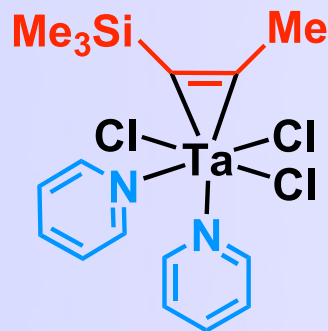
r.t., 3 h, 93%



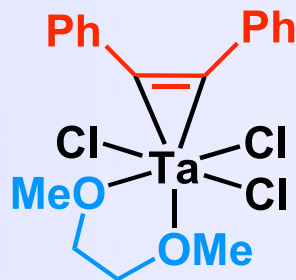
r.t., 4.5 h, 88%



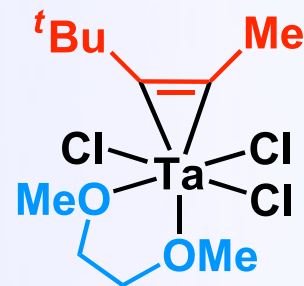
60 °C, 1 h, 64%



r.t., 96 h, 82%



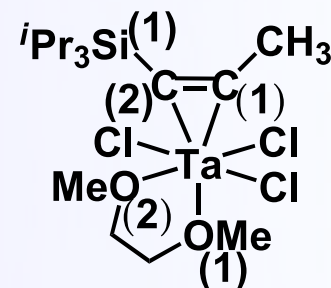
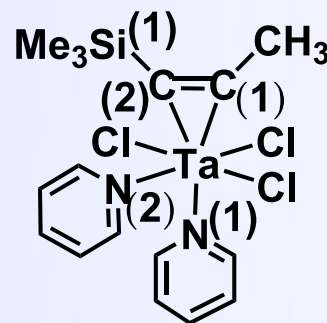
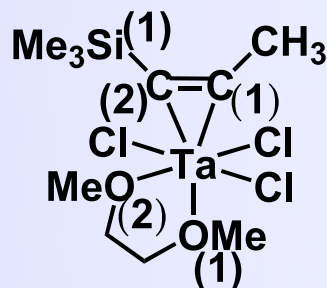
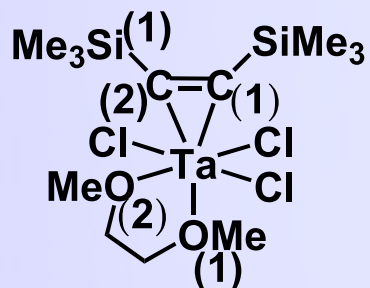
100 °C, 3 h, 0%^a



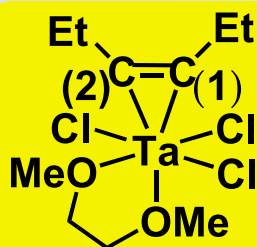
r.t., 36 h, 18%

^a toluene- d_8 was used.

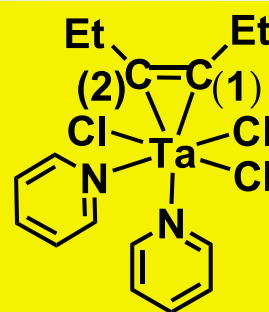
タンタルーシリルアルキン錯体の構造パラメータ



Ta–C(1)	2.068(8) Å	2.05(2) Å	2.08(1) Å	2.051(9) Å
Ta–C(2)	2.077(5) Å	2.11(1) Å	2.06(1) Å	2.090(8) Å
Ta–O(1)	2.357(4) Å	2.34(1) Å		2.332(7) Å
Ta–O(2)	2.183(4) Å	2.21(1) Å		2.240(6) Å
Ta–N(1)			2.44(1) Å	
Ta–N(2)			2.30(1) Å	
C(1)–C(2)	1.326(8) Å	1.32(2) Å	1.32(2) Å	1.32(1) Å
C(1)–C(2)–Si(1)	139.8(5) deg.	140(1) deg.	136(1) deg.	142.6(7) deg.

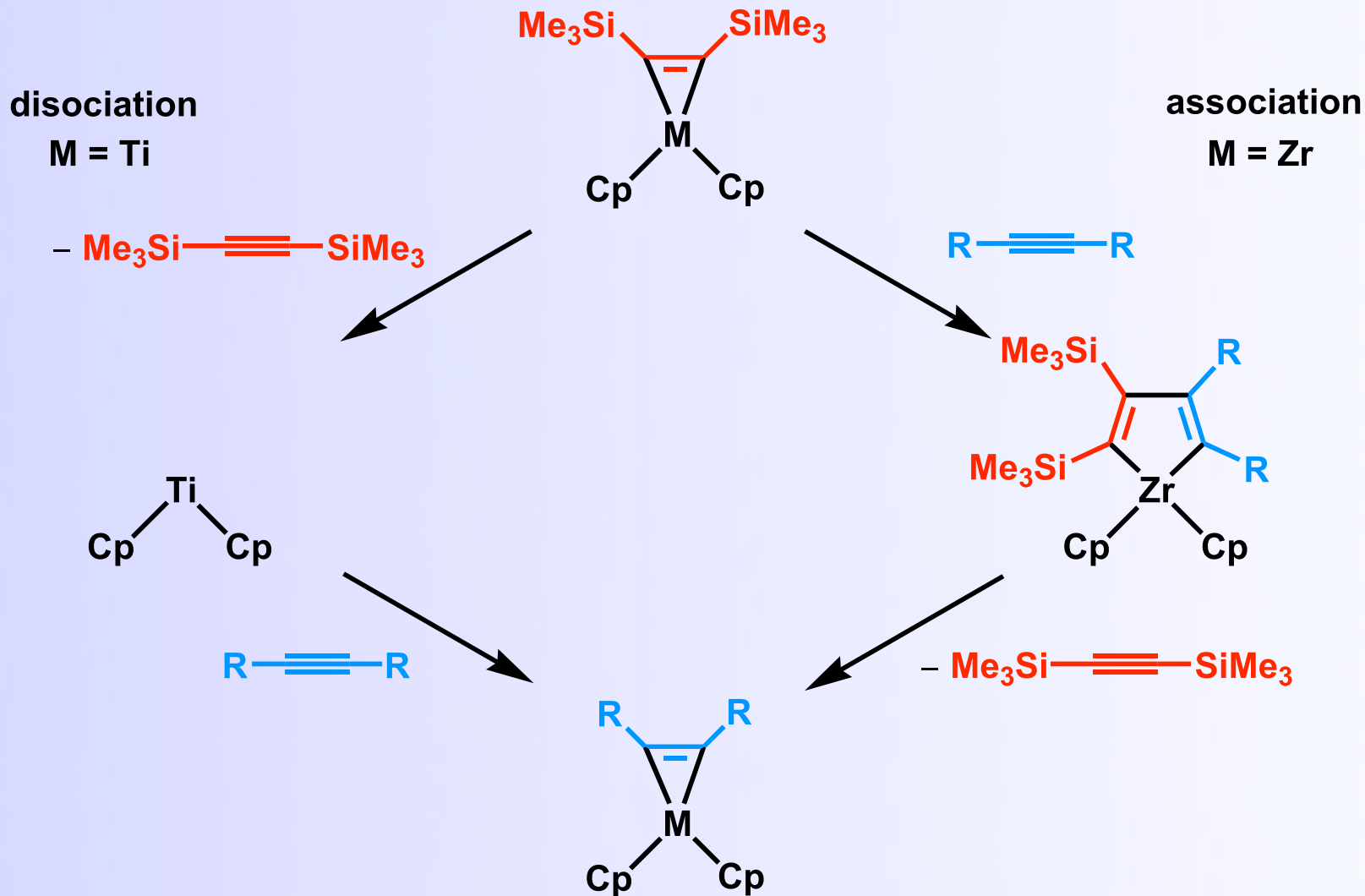


Ta–C(1)	2.046(9) Å
Ta–C(2)	2.102(7) Å



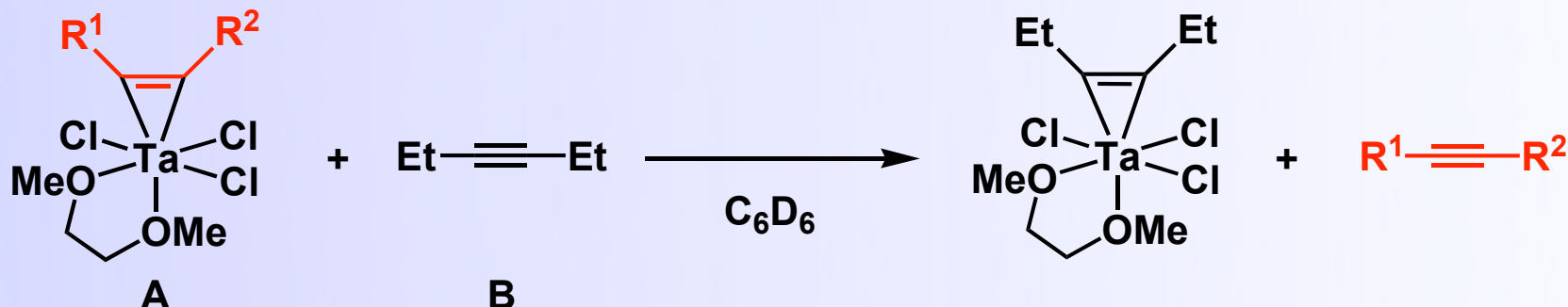
Ta–C(1)	2.04(1) Å
Ta–C(2)	2.07(1) Å

4族アルキン交換反応の推定メカニズム



Rosenthal, U.; Burlakov, V. V.; Baumann, W. P.; Spannenberg, A. *Organometallics* **2003**, 22, 884.
 Horacek, M.; Kupfer, V.; Thewalt, U.; Stepnicka, P.; Polasek, M.; Mach, K. *Organometallics* **1999**, 18, 3572.
 Mansel, S.; Thomas, D.; Lefeber, C.; Heller, D.; Kempe, R.; Baumann, W.; Rosenthal, U. *Organometallics* **1997**, 16, 2886.

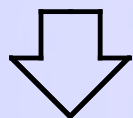
反応速度と活性化パラメータの算出



反応速度

$$\text{rate} = k[A]^m[B]^n$$

擬一次反応条件
(反応系中に B を過剰量加える)



[B] >> [A] であるので、[B] を定数とみなすことができる

$$k_{\text{obs}} = k[B]^n$$

$$\text{rate} = k_{\text{obs}}[A]^m$$

活性化パラメータの算出

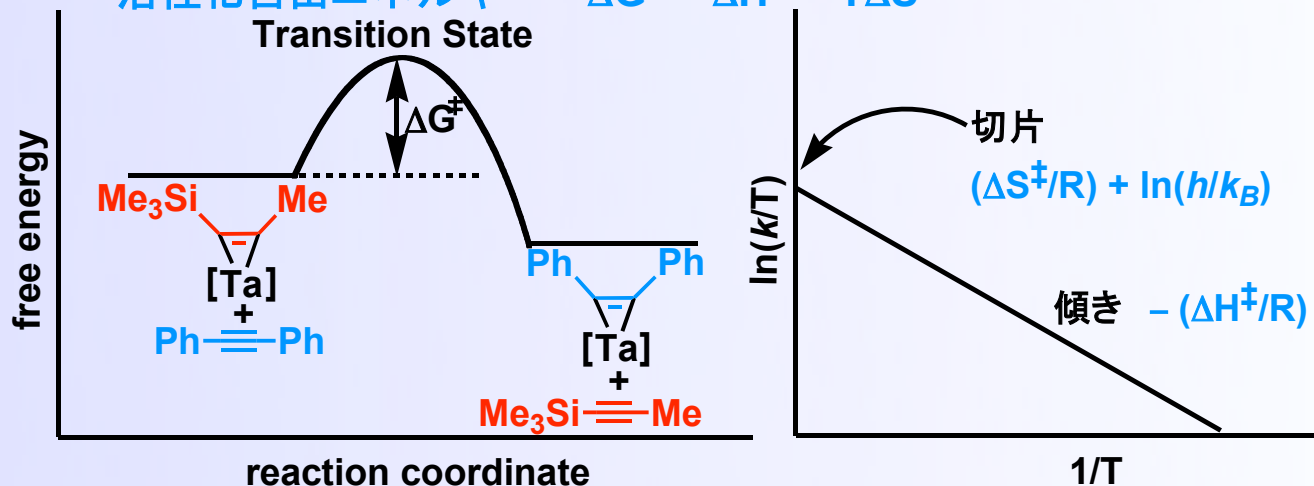
Eyring の式 $\ln(k/T) = -(\Delta H^\ddagger/R)(1/T) + (\Delta S^\ddagger/R) + \ln(h/k_B)$

測定値 k: 反応速度定数, T: 測定温度

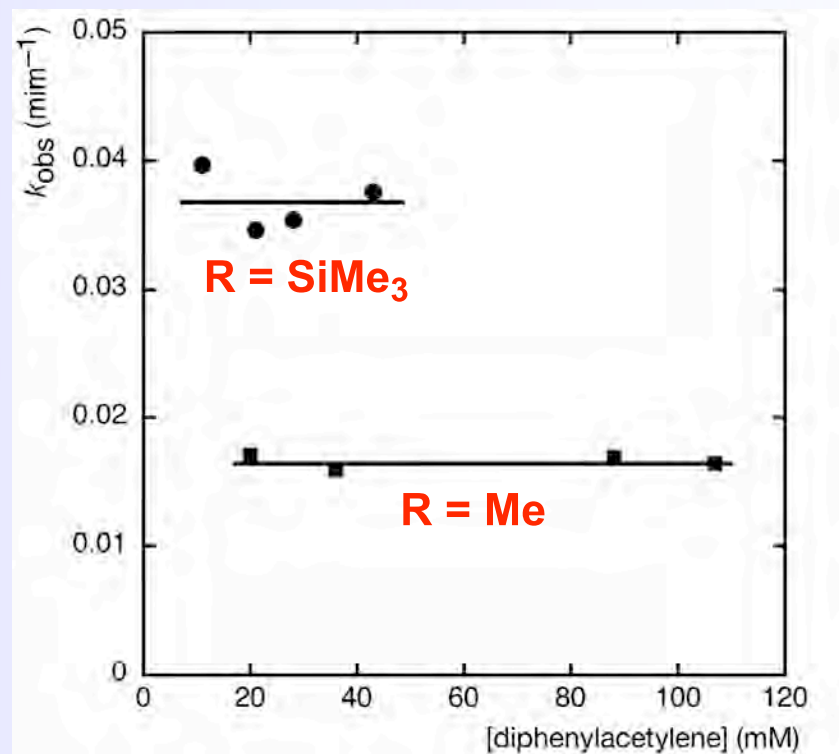
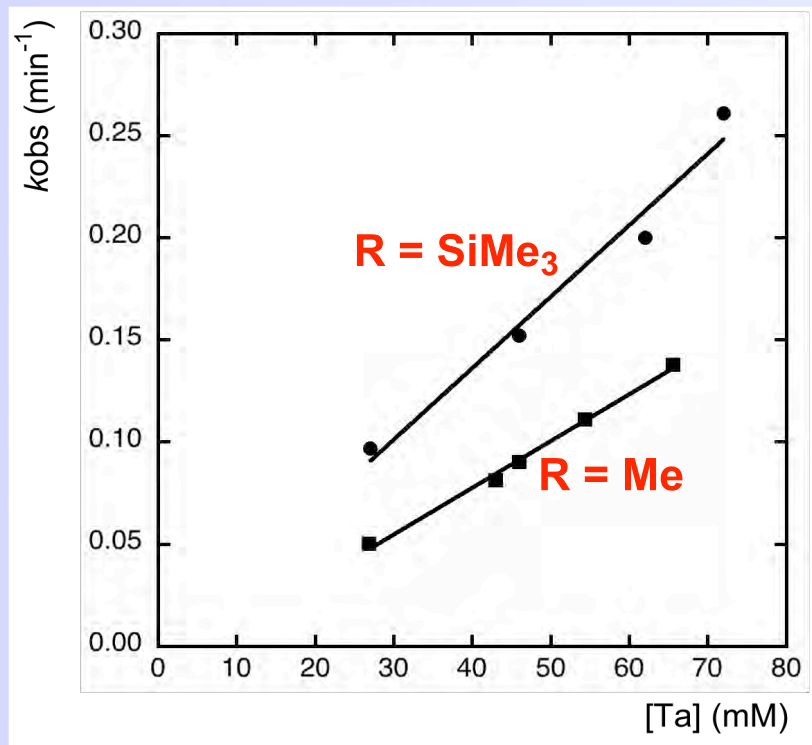
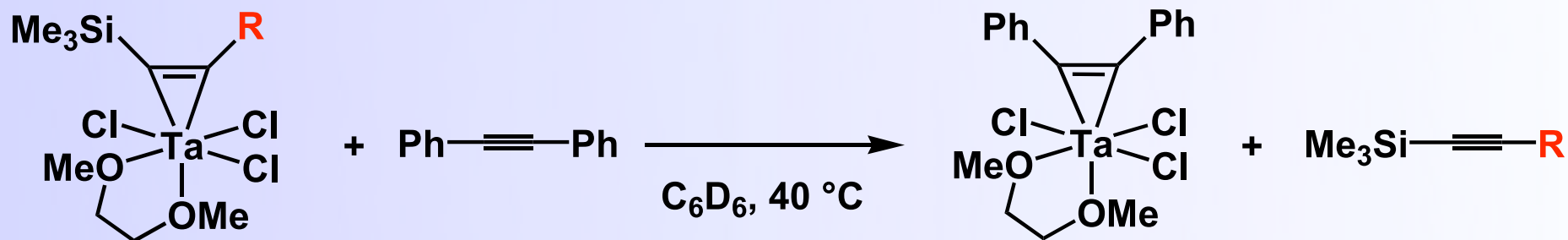
定数 R: 気体定数, h: プランク定数, k_B: ボルツマン定数

ΔH^\ddagger : 活性化エンタルピー, ΔS^\ddagger : 活性化エントロピー

活性化自由エネルギー $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$

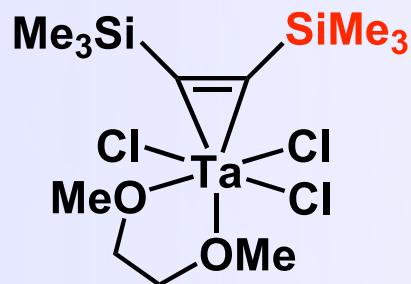
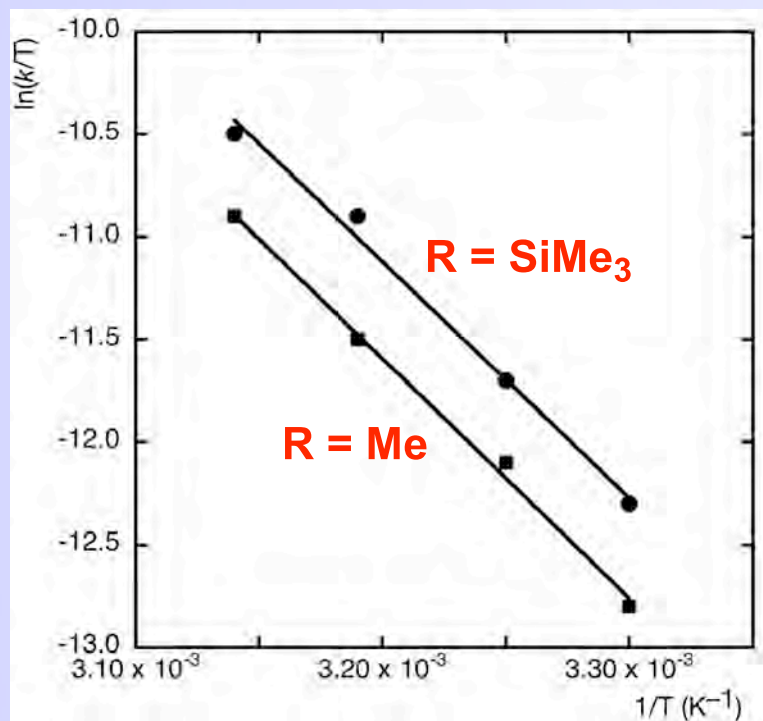
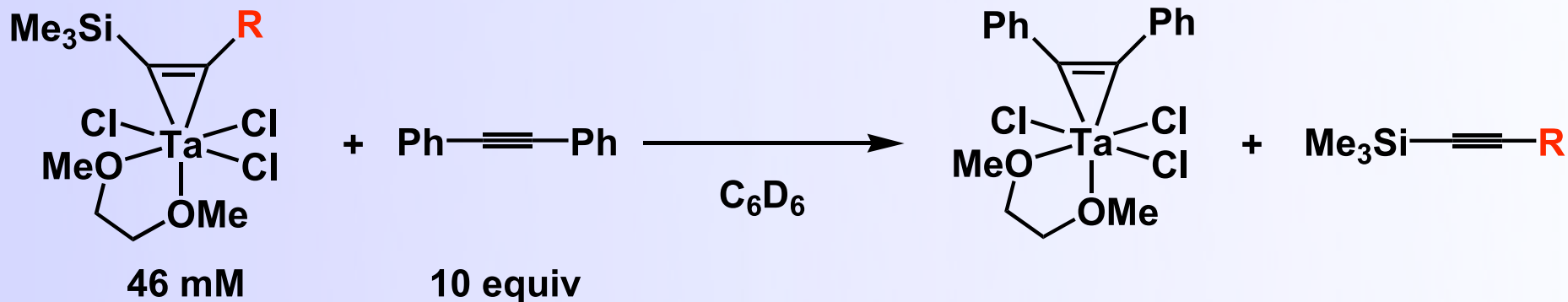


DME錯体の速度式

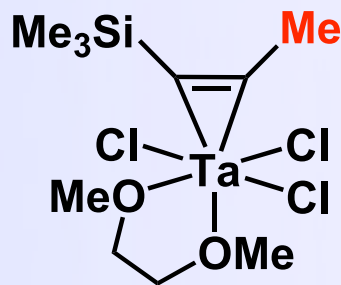


$$v = k[\text{Ta complex}]$$

DME錯体の活性化パラメータ



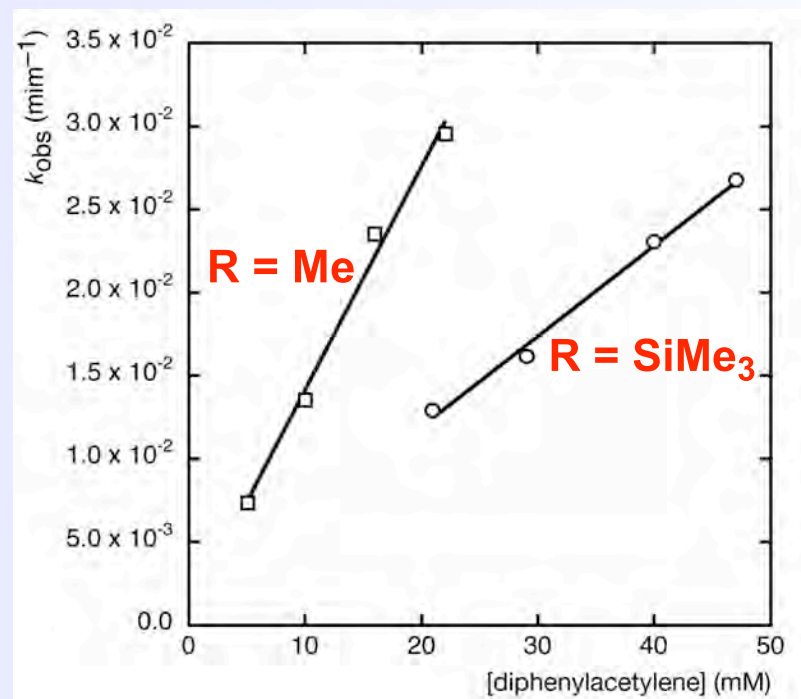
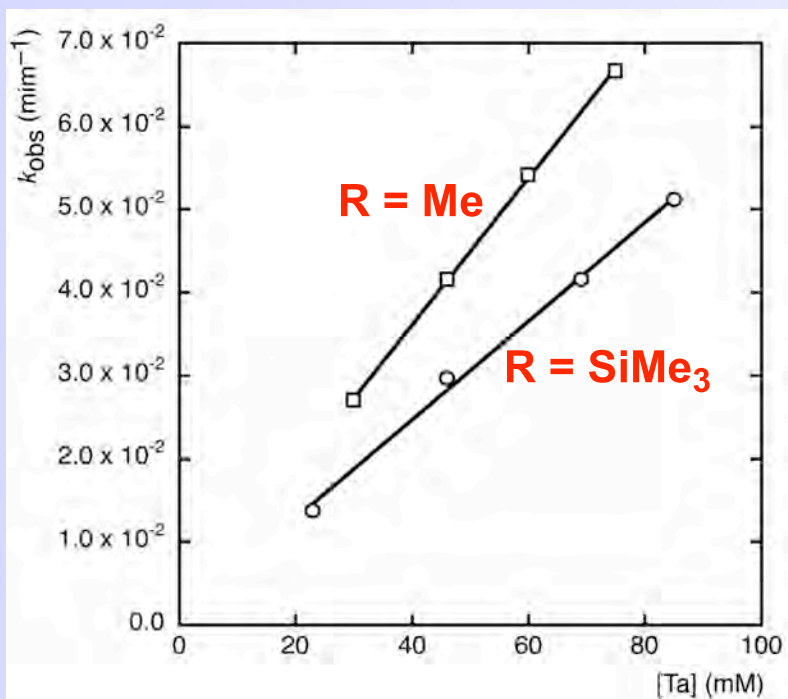
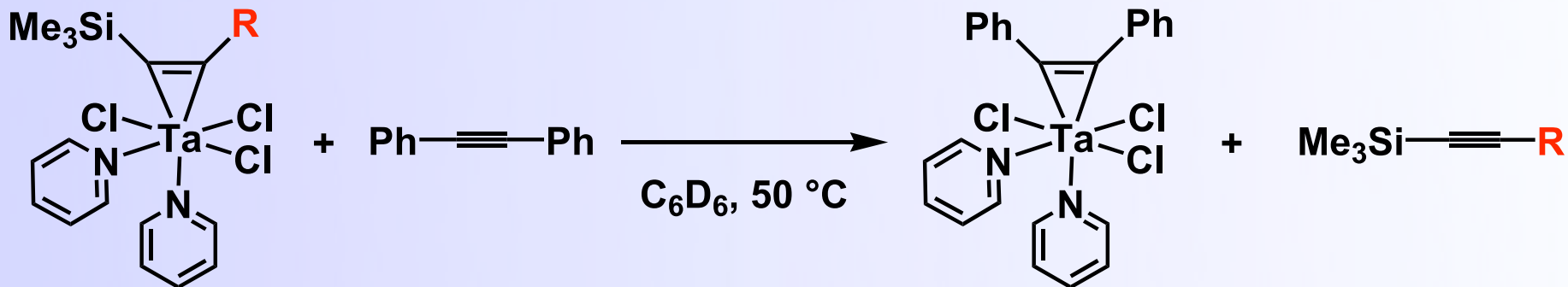
$$\begin{aligned}
 \Delta G^\ddagger &= +85 \pm 6 \text{ (kJ mol}^{-1}\text{)}^a \\
 \Delta H^\ddagger &= +98 \pm 6 \text{ (kJ mol}^{-1}\text{)} \\
 \Delta S^\ddagger &= +44 \pm 15 \text{ (J K}^{-1}\text{mol}^{-1}\text{)}
 \end{aligned}$$



$$\begin{aligned}
 \Delta G^\ddagger &= +92 \pm 4 \text{ (kJ mol}^{-1}\text{)}^a \\
 \Delta H^\ddagger &= +100 \pm 4 \text{ (kJ mol}^{-1}\text{)} \\
 \Delta S^\ddagger &= +26 \pm 13 \text{ (J K}^{-1}\text{mol}^{-1}\text{)}
 \end{aligned}$$

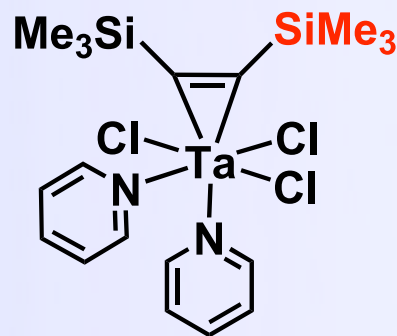
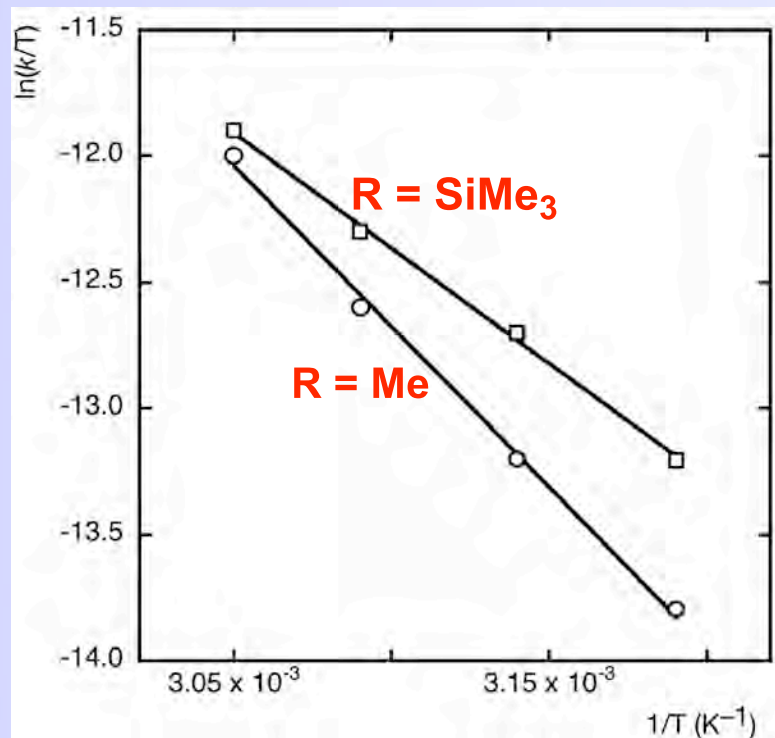
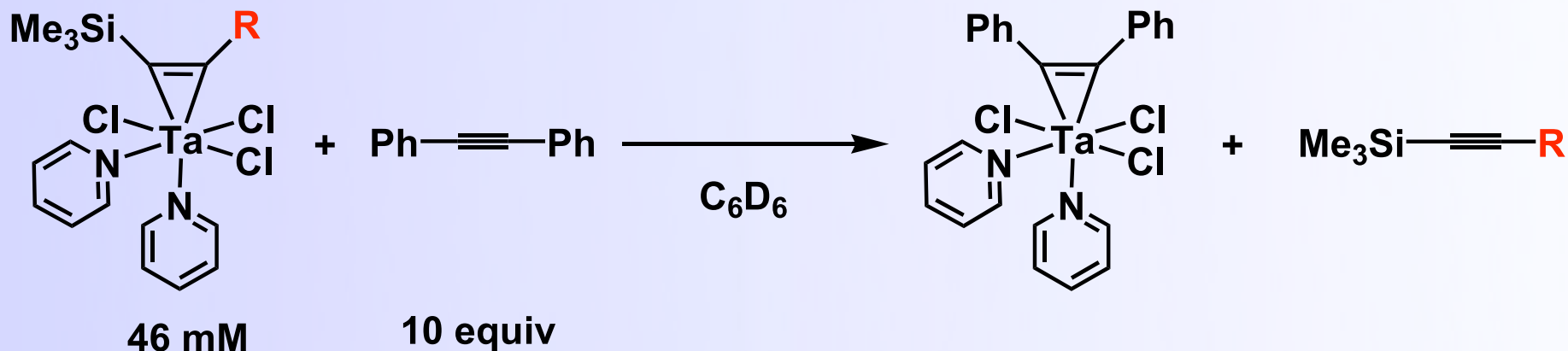
^a 298.15K

ピリジン錯体の速度式

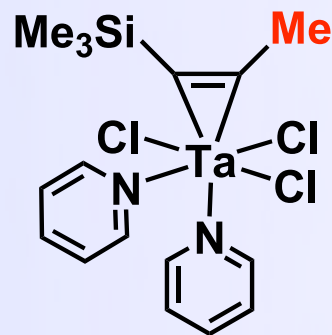


$$v = k[\text{Ta complex}][\text{alkyne}]$$

ピリジン錯体の活性化パラメータ



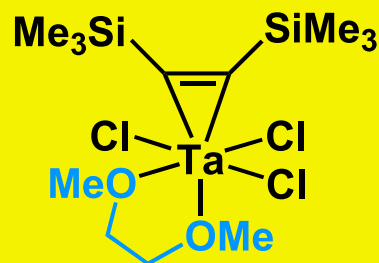
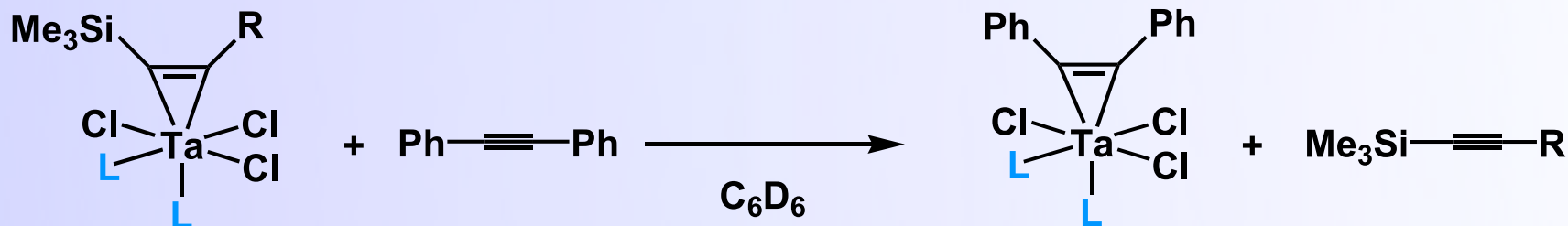
$\Delta G^\ddagger = +98 \pm 0 \text{ (kJ mol}^{-1}\text{)}^a$
 $\Delta H^\ddagger = +97 \pm 0 \text{ (kJ mol}^{-1}\text{)}$
 $\Delta S^\ddagger = -1.5 \pm 1.2 \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$



$\Delta G^\ddagger = +95 \pm 3 \text{ (kJ mol}^{-1}\text{)}^a$
 $\Delta H^\ddagger = +76 \pm 3 \text{ (kJ mol}^{-1}\text{)}$
 $\Delta S^\ddagger = -64 \pm 9 \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$

^a 298.15K

アルキン交換反応の速度式と活性化パラメータ

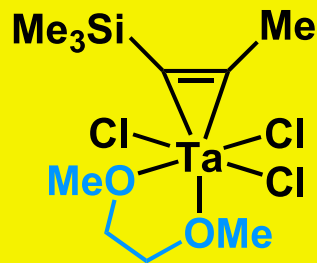


$$v = k[\text{Ta complex}]$$

$$\Delta G^\ddagger = +85 \pm 6 \text{ (kJ mol}^{-1}\text{)}^a$$

$$\Delta H^\ddagger = +98 \pm 6 \text{ (kJ mol}^{-1}\text{)}$$

$$\Delta S^\ddagger = +44 \pm 15 \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$$

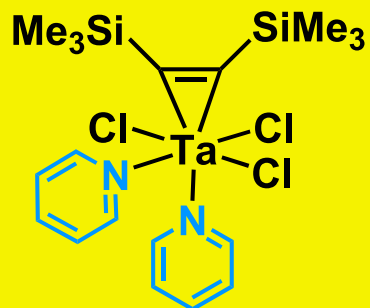


$$v = k[\text{Ta complex}]$$

$$\Delta G^\ddagger = +92 \pm 4 \text{ (kJ mol}^{-1}\text{)}^a$$

$$\Delta H^\ddagger = +100 \pm 4 \text{ (kJ mol}^{-1}\text{)}$$

$$\Delta S^\ddagger = +26 \pm 13 \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$$

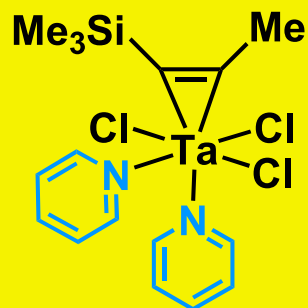


$$v = k[\text{Ta complex}][\text{alkyne}]$$

$$\Delta G^\ddagger = +98 \pm 0 \text{ (kJ mol}^{-1}\text{)}^a$$

$$\Delta H^\ddagger = +97 \pm 0 \text{ (kJ mol}^{-1}\text{)}$$

$$\Delta S^\ddagger = -1.5 \pm 1.2 \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$$



$$v = k[\text{Ta complex}][\text{alkyne}]$$

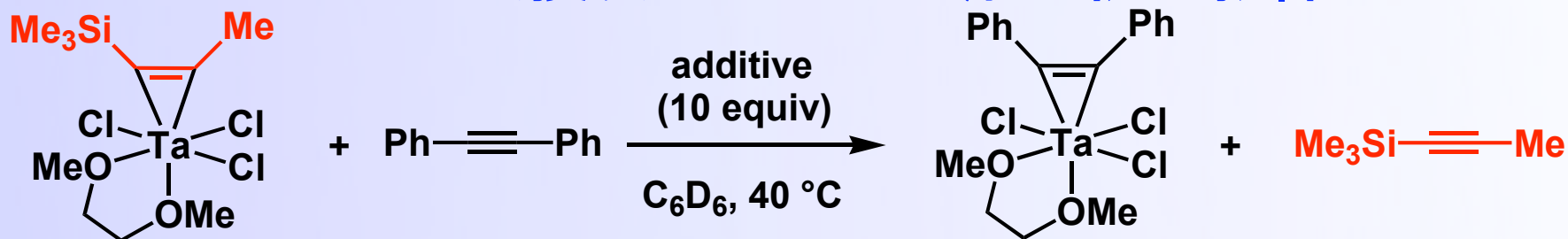
$$\Delta G^\ddagger = +95 \pm 3 \text{ (kJ mol}^{-1}\text{)}^a$$

$$\Delta H^\ddagger = +76 \pm 3 \text{ (kJ mol}^{-1}\text{)}$$

$$\Delta S^\ddagger = -64 \pm 9 \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$$

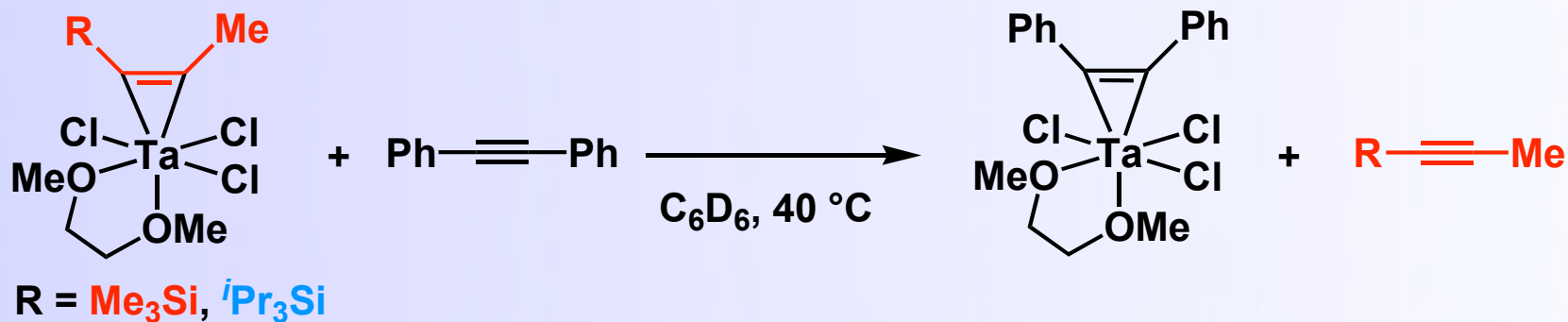
^a 298.15K

アルキン交換反応における添加物の影響



additive	$k_{\text{obs}}[\text{min}^{-1}]$
none	0.0904
$\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{Me}$	0.0456
DME	no reaction
-O-Me	0.0239

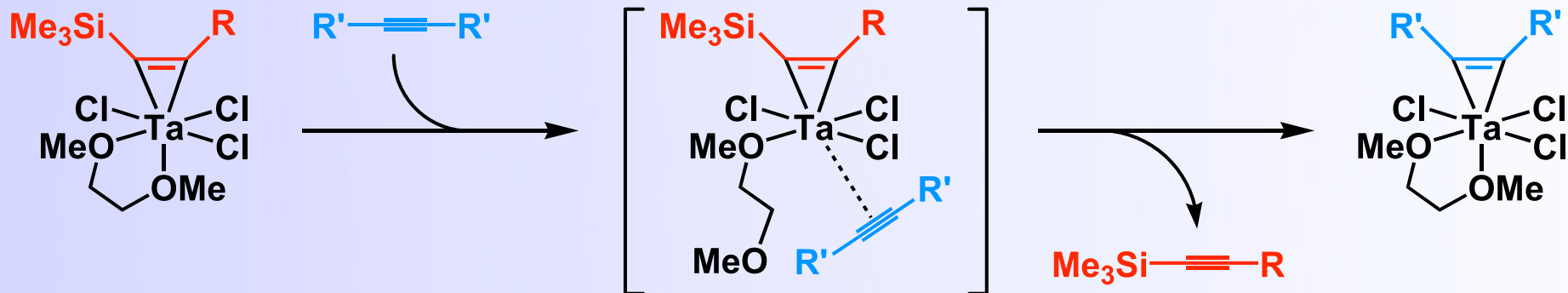
アルキン交換反応におけるアルキン部位の嵩高さの影響



$\text{R} = \text{Me}_3\text{Si}, k_{\text{obs}} = 9.04 \times 10^{-2} \text{ min}^{-1}$

$\text{R} = ^i\text{Pr}_3\text{Si}, k_{\text{obs}} = 17.3 \times 10^{-2} \text{ min}^{-1}$

アルキン交換反応の推定メカニズム



R = SiMe₃: $v = k[\text{Ta complex}]$

$$\Delta G^\ddagger = +85 \pm 6 \text{ (kJ mol}^{-1}\text{)}^a$$

$$\Delta H^\ddagger = +98 \pm 6 \text{ (kJ mol}^{-1}\text{)}$$

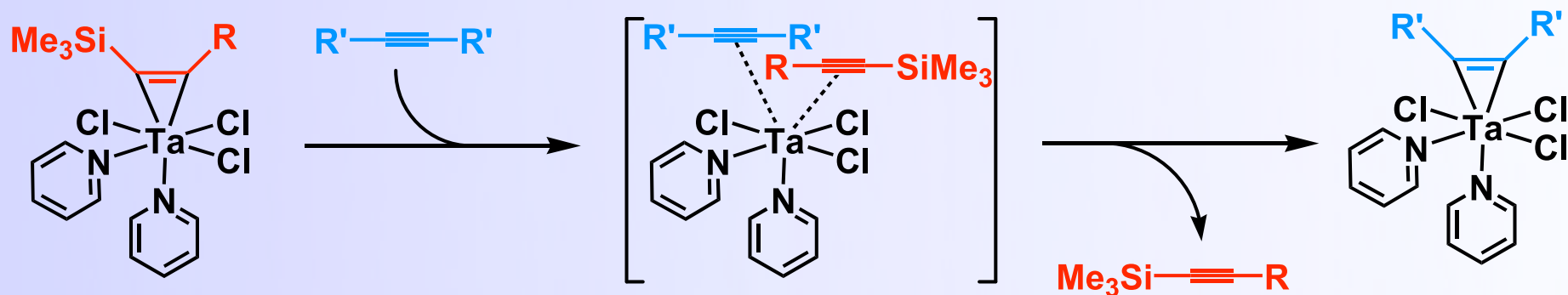
$$\Delta S^\ddagger = +44 \pm 15 \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$$

R = Me: $v = k[\text{Ta complex}]$

$$\Delta G^\ddagger = +92 \pm 4 \text{ (kJ mol}^{-1}\text{)}^a$$

$$\Delta H^\ddagger = +100 \pm 4 \text{ (kJ mol}^{-1}\text{)}$$

$$\Delta S^\ddagger = +26 \pm 13 \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$$



R = SiMe₃: $v = k[\text{Ta complex}][\text{alkyne}]$

$$\Delta G^\ddagger = +98 \pm 0 \text{ (kJ mol}^{-1}\text{)}^a$$

$$\Delta H^\ddagger = +97 \pm 0 \text{ (kJ mol}^{-1}\text{)}$$

$$\Delta S^\ddagger = -1.5 \pm 1.2 \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$$

R = Me: $v = k[\text{Ta complex}][\text{alkyne}]$

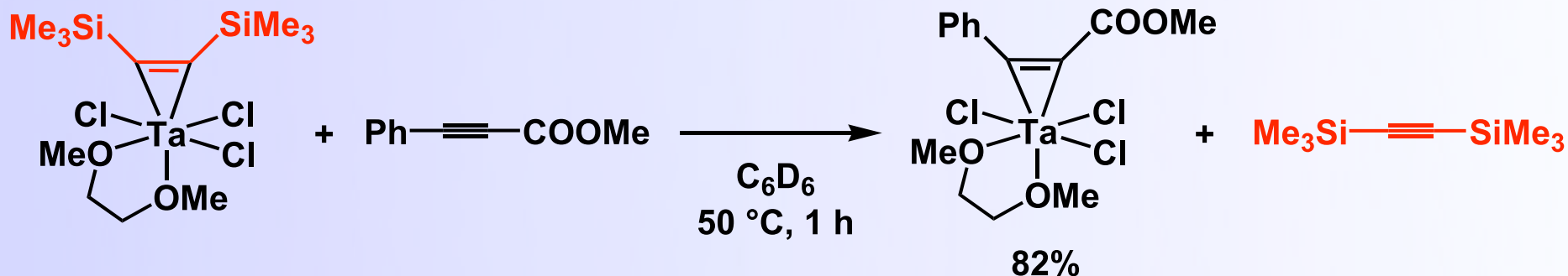
$$\Delta G^\ddagger = +95 \pm 3 \text{ (kJ mol}^{-1}\text{)}^a$$

$$\Delta H^\ddagger = +76 \pm 3 \text{ (kJ mol}^{-1}\text{)}$$

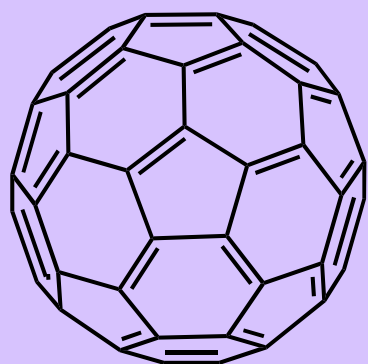
$$\Delta S^\ddagger = -64 \pm 9 \text{ (J K}^{-1}\text{mol}^{-1}\text{)}$$

^a 298.15K

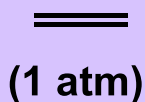
様々な不飽和化合物とのアルキン交換反応の検討



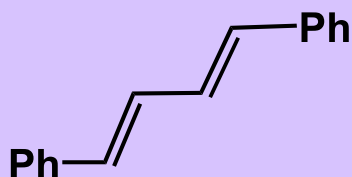
アルキン交換が進行しなかった化合物



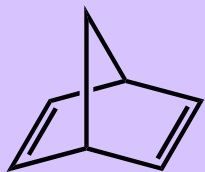
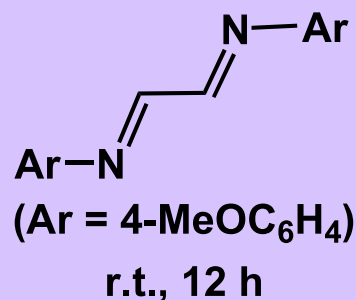
100 °C, 7 h



r.t., 5 d



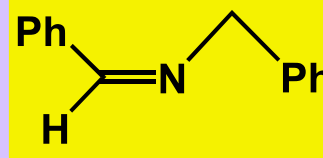
100 °C, 7 h



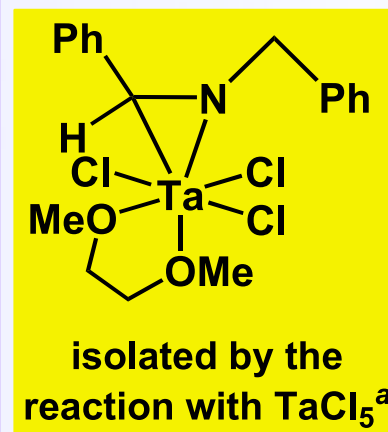
50 °C, 18 h



50 °C, 16 h



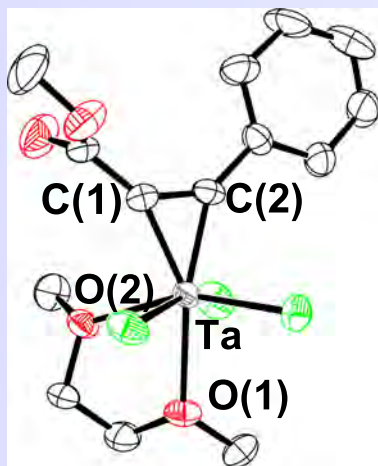
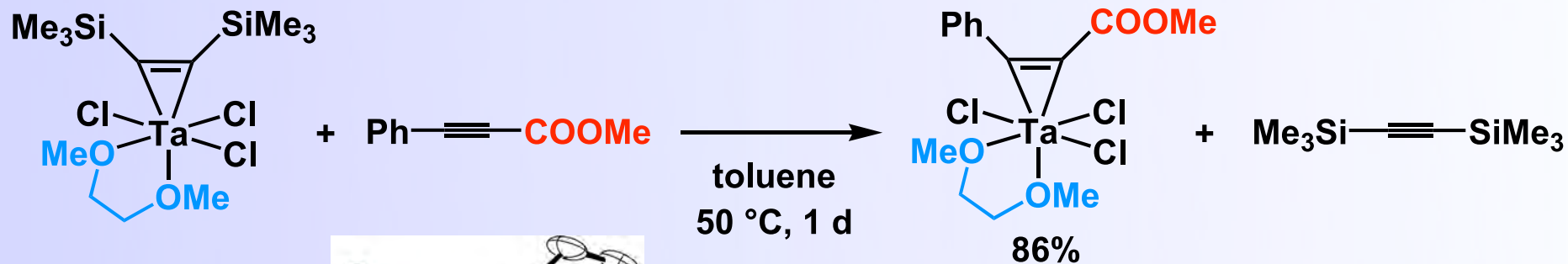
50 °C, 16 h



^a Takai, K.; Ishiyama, T.; Yasue, H.; Nobunaka, T.; Itoh, M.; Oshiki, T.; Mashima, K.; Tani, K. *Organometallics* **1998**, 17, 5128.

アルキン交換反応の新規錯体合成への応用

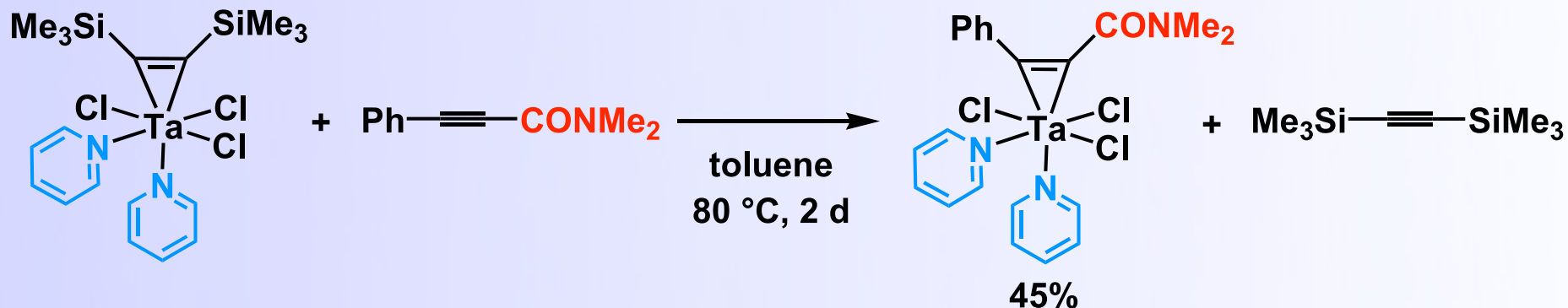
エステル置換基をもつタンタルーアルキン錯体の合成



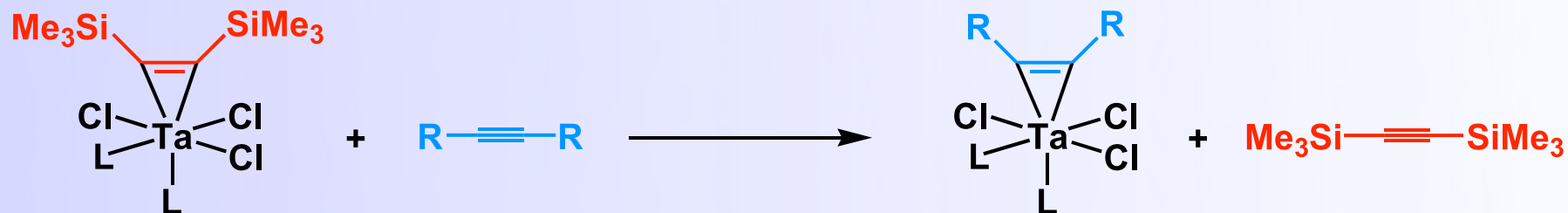
構造パラメータ

Ta-C(1)	2.068(8) Å
Ta-C(2)	2.077(5) Å
C(1)-C(2)	1.326(8) Å
Ta-O(1)	2.068(8) Å
Ta-O(2)	2.077(5) Å

アミド置換基をもつタンタルーアルキン錯体の合成

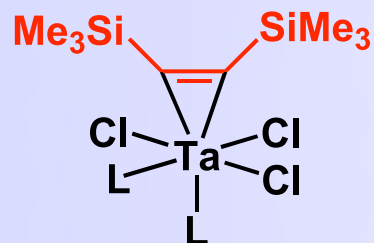
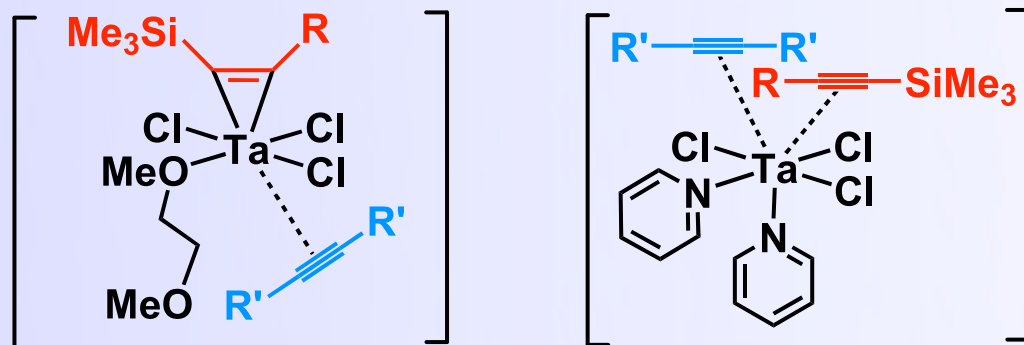


まとめ



$\text{L}_2 = \text{dme}$

$\text{L} = \text{py}$



$\text{Ph}-\text{C}\equiv\text{C}-\text{COOMe}$

$\text{L}_2 = \text{dme}$

$\text{Ph}-\text{C}\equiv\text{C}-\text{COOMe}$

$\text{L} = \text{py}$

